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Solvent effects in time-dependent self-consistent field methods II: variational formulations and analytical gradients

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This study describes variational energy expressions and analytical excited state energy gradients for time-dependent self-consistent field methods with polarizable solvent effects. Linear response, vertical excitation, and state-specific solvent models are examined. Enforcing a variational ground state energy expression in the state-specific model is found to reduce it to the vertical excitation model. Variational excited state energy expressions are then provided for the linear response and vertical excitation models and analytical gradients are formulated. Using semiempirical model chemistry, the variational expressions are verified by numerical and analytical differentiation with respect to a static external electric field. Analytical gradients are further tested by performing microcanonical excited state molecular dynamics with *p*-nitroaniline.

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I. INTRODUCTION

Analytical energy gradients for time-dependent self-consistent field (TD-SCF) methods, ranging from time-dependent Hartree Fock (TD-HF) to time-dependent density functional theory (TD-DFT), allow excited state molecular dynamics (ESMD) and geometry optimizations to be performed efficiently for large systems.¹⁻⁷ Specifically, analytical gradients allow for efficient computation of forces by eliminating the need to calculate derivatives of density matrices or wavefunctions.⁸⁻¹⁸ This requires a variational formulation of the excited state (ES) energy.¹⁹⁻²⁵ Although already formulated for the gas phase,²⁶ variational formulations and analytical gradients for TD-SCF methods when solvent effects are present have not been fully explored. Including solvent effects in these calculations has the benefit of better describing states which are significantly affected by solvation, including those with charge-transfer (CT) character.²⁷⁻²⁹

Solvent effects for the ES can be simulated using several models in TD-SCF methods. In the linear response (LR) model, the solvent is polarized by the transition density.³⁰⁻³² Therefore, it is best applied to solvent effects for excitations with significant transition dipole (bright states) or higher order transition multipoles. In the vertical excitation (VE)³³⁻³⁸ and state-specific (SS)^{39,40} models, the solvent is polarized by the ES charge density and is thus best applied to states with CT character. For calculations of ES properties, the VE model can be thought of as an approximation to the latter which, as shown in this study, allows for a variational formulation. This approximation is the neglect of SS solvent effects in the ground state (GS) self-consistent field (SCF) equation. Further information and comparisons between these models is available in Ref. 41.

Analytical gradients were formulated some years ago for the LR model in TD-SCF and other methods.^{30,42,43} However, with the LR model, the time-dependent Stokes shift and thus fluorescence solvatochromism cannot be described accurately because of the lack of direct interaction between the solvent and ES charge density.^{40,44-47} This is because accurate simulations of fluorescence solvatochromism requires relaxation of the molecular structure on the ES potential energy surface.^{27,48-50} This has not yet been feasible with SS or VE methods in TD-SCF theories for large molecules due to the lack of analytical gradients. As a result, simulations of ES solvent effects in many important systems have not been performed. The analytical gradient of the VE model in equations of motion coupled cluster theory³⁵

and the SS model in symmetry-adapted cluster-configuration interaction theory have been formulated³⁶ but are not suitable for the simulation of ESMD with large systems because of the high computational cost of the underlying quantum chemical method. Formulation of a variational ES energy from TD-SCF methods is required for ESMD of large systems and relevant time scales.⁴⁹

The ES energy cannot be obtained directly from TD-SCF methods. Instead, it is determined from the addition of the excitation energy to the GS energy. The major issue for a variational formulation of the ES energy is that the excitation energy does not result from an expression that is variational with respect to the GS density matrix \mathbf{P} . However, the Z-vector technique can be used to formulate a variational expression after the excitation energies have been calculated.²⁶ The ES density matrix that is the result of a variational ES energy expression is described as the so-called relaxed density matrix. It is determined using Lagrange multipliers in a free energy functional. When the VE model is used, the variational formulation of the ES energy is modified substantially from vacuum. Here, we clearly outline the process of obtaining the variational ES energy for the VE model in this publication. It is also found that a similar formulation is not possible for the SS model. For completeness, we show this by examining the effects of the SS model on variation of the GS electronic energy.

The GS electronic energy in vacuum obeys the Hartree-Fock (HF) or Kohn-Sham (KS) variational principle.^{24,51,52} The effective potential of a polarizable solvent from the LR or VE model is mathematically similar to the Hartree potential in vacuum and the GS electronic energy calculated with these methods is also variational. On the other hand, using the SS model in TD-SCF methods breaks the variational principle for the GS electronic energy. Interestingly, it is found that upon enforcing the condition that the GS energy expression is variational while using the SS model, it is reduced to the VE model. Essential elements of the SS model are lost in this variational formulation, such that the derived analytical gradients would not reflect the original formulation for single-point calculations. Thus, after discussing the SS model, we formulate analytical gradients for only the LR and VE models.

This publication is outlined as follows. In section II, the GS variational principle is examined for the SS model. In section III, the necessary manipulations to provide variational excitation energy expressions are described using the vacuum formalism and extended to the LR and VE models. In section IV the Z-vector technique is applied to give variational ES

energies. In section V, analytical energy gradients for vacuum, LR, and VE models are given using the results of sections III and IV. In section VI, numerical results are provided for two examples. First, the gradient of the excitation energy with respect to a static electric field is used to test the Z-vector formulations. Then, the ultrafast dynamics in solution of a state with CT character are explored to test the analytical ES energy gradients. Semiempirical model chemistry, specifically the AM1 model, is used for these simulations.⁵² Conclusions are presented in section VII.

II. GROUND STATE VARIATIONAL ENERGY EXPRESSION

In a HF or KS calculation without solvent effects, the GS electronic energy E_{gr} is a variational quantity.^{53,54} This holds true not only for calculations in vacuum, but also with either the LR model or the VE model, since they both use the same Fock-like operator which has similar structure to the standard calculations in vacuum.^{33,55} This does not hold for the SS model because the Fock-like operator has been modified with quantities calculated from the TD-SCF equations.^{39,41} So far, a variational formulation of the ES energy with the SS model has not been found. The difficulty can be made clear by examining E_{gr} using the following optimization process that ensures stationarity with respect to variation of all GS and ES density matrices.

A free energy functional \mathcal{F} corresponding to E_{gr} can be written as

$$\mathcal{F}(\phi, \lambda) = \sum_{\mu \in occ} \langle \phi_\mu | \mathbf{t} + \frac{1}{2} \mathbf{V}(\mathbf{P}) | \phi_\mu \rangle + \sum_{\mu, \nu \in occ} \lambda_\mu [\delta_{\mu\nu} - \langle \phi_\mu | \phi_\nu \rangle] \quad (1)$$

where $\mathbf{P} = \sum_{\mu \in occ} |\phi_\mu\rangle\langle\phi_\mu|$ is the GS single electron density matrix and $t_{ij\sigma}$ are one-electron integrals accounting for the kinetic energy and nuclear attraction of an electron. μ is the molecular orbital index. Here and throughout the main body of this manuscript, an orthogonal atomic orbital basis is assumed. This could be performed, for instance, by Löwdin decomposition of the overlap matrix \mathbf{S} .⁵⁴ Moreover, expressions for the working equations in a nonorthogonal basis are given in Appendix A. The elements of the operator $\mathbf{V}(\mathbf{x})$ acting on an arbitrary density matrix \mathbf{x} are given by

$$V_{ij\sigma}(\mathbf{x}) = J_{ij\sigma}(\mathbf{x}) - K_{ij\sigma}(\mathbf{x}) + v_{ij\sigma}^{xc}(\mathbf{x}) \quad (2)$$

where $\mathbf{v}^{xc}(\mathbf{x})$ is the exchange-correlation potential (i.e. the functional derivative of the exchange-correlation action)⁵³ and the Hartree and exchange terms are represented as

$$J_{ij\sigma}(\mathbf{x}) - K_{ij\sigma}(\mathbf{x}) = \sum_{kl\sigma'} (ij\sigma | kl\sigma') x_{kl\sigma'} - c_x (ik\sigma | jl\sigma') x_{kl\sigma} \delta_{\sigma\sigma'}. \quad (3)$$

The parameter c_x allows mixing of pure DFT and HF theories, e.g. in the case of Becke’s hybrid functionals.^{56–58} The indices i, j, k, l and σ refer to the spatial and spin indices, respectively, and $(ij\sigma | kl\sigma')$ are conventional two-electron integrals representing Coulombic interactions.

In Eq. 1, the Lagrange multipliers λ_μ ensure the orthonormality of the molecular orbitals ϕ_μ . Upon optimization of Eq. 1, they are equivalent to the molecular orbital energies for the GS. When \mathcal{F} is minimized with respect to ϕ_μ , only variation of either bra or ket is necessary because $|\phi_\mu\rangle$ and $\langle\phi_\mu|$ are complex conjugates. For the vacuum formulation, this optimization results in,

$$\mathbf{F}(\mathbf{P})|\phi_\mu\rangle = \lambda_\mu|\phi_\mu\rangle. \quad (4)$$

The standard Fock or KS matrix without solvent effects is given by

$$\mathbf{F}(\mathbf{P}) = \mathbf{t} + \mathbf{V}(\mathbf{P}). \quad (5)$$

Eq. 4 is the GS SCF equation. The GS SCF energy, $E_{scf} = \sum_{\mu \in occ} \lambda_\mu$, is not a variational quantity. Half of the electron-electron interaction must be subtracted to obtain E_{gr} . This is clearly seen by multiplying Eq. 4 from the right by $\langle\phi_\mu|$, summing over the occupied molecular orbitals, and inserting the result in Eq. 1. Upon optimization, the free energy functional is equivalent to E_{gr} ,

$$\mathcal{F}_{opt} = E_{gr} = E_{scf} - \frac{1}{2} \sum_{\mu \in occ} \langle\phi_\mu|\mathbf{V}(\mathbf{P})|\phi_\mu\rangle. \quad (6)$$

When applying Eq. 1 to the Fock-like operators which use either the LR or VE model, the modified \mathbf{F} is given by

$$\mathbf{F}_{LR}(\mathbf{P}) = \mathbf{F}(\mathbf{P}) + \mathbf{V}_S(\mathbf{P}). \quad (7)$$

The effective solvent potential $\mathbf{V}_S(\mathbf{x})$ can be calculated using any method that can be treated in the same way as the Hartree potential. Examples are the polarizable continuum model (PCM)⁵⁹ or polarizable QM/MM methods.⁶⁰ Since LR and VE models use the GS density

matrix in this effective potential, it has similar properties to $\mathbf{V}(\mathbf{P})$ and is treated in a same manner in Eqs. 5 and 6.

On the other hand, the SS model, which uses the modified \mathbf{F} given by

$$\mathbf{F}_{SS}(\mathbf{P}) = \mathbf{F}(\mathbf{P}) + \mathbf{V}_S(\bar{\mathbf{P}}_k) \quad (8)$$

breaks the necessary stationarity of E_{gr} . Here, $\bar{\mathbf{P}}_k = \mathbf{P} + \mathbf{T}_k$ is the so-called unrelaxed single electron density matrix for ES k and \mathbf{T}_k is the so-called unrelaxed difference between the GS and ES single electron density matrices.^{6,41,61} The term which must be examined is $\mathbf{V}_S(\mathbf{T}_k)$. \mathbf{T}_k is a function of the transition density matrix, $\boldsymbol{\xi}_k$, and \mathbf{P} ,⁶¹

$$\mathbf{T}_k = [[\boldsymbol{\xi}_k^\dagger, \mathbf{P}], \boldsymbol{\xi}_k]. \quad (9)$$

when the occupied block of \mathbf{P} is equivalent to the identity matrix \mathbf{I} . The structure of $\boldsymbol{\xi}_k$ is described in detail in Sec. III. We replace \mathbf{F} with \mathbf{F}_{SS} in Eq. 1 to give the functional \mathcal{F}_{SS} and set the derivative with respect to $\boldsymbol{\xi}_k$ to zero. This condition equates to

$$\frac{\partial \mathcal{F}_{SS}}{\partial \boldsymbol{\xi}_k} = [\mathbf{V}_S(\mathbf{P}), \boldsymbol{\xi}_k] = 0. \quad (10)$$

where the matrix elements of a scalar (k) by matrix partial derivative are given by $(\partial k / \partial \mathbf{x})_{nm} = \partial k / \partial x_{nm}$.

To illustrate the significance of this result, we multiply Eq. 10 from the left by $\langle \xi_k |$. This can be written as

$$\langle \xi_k | [\mathbf{V}_S(\mathbf{P}), \boldsymbol{\xi}_k] \rangle = \text{Tr}(\mathbf{T}_k \mathbf{V}_S(\mathbf{P})) = \text{Tr}(\mathbf{P} \mathbf{V}_S(\mathbf{T}_k)) = \sum_{\mu \in occ} \langle \phi_\mu | \mathbf{V}_S(\mathbf{T}_k) | \phi_\mu \rangle = 0. \quad (11)$$

where we have used the cyclic invariance of the trace given by $((\text{Tr}(\mathbf{x}\mathbf{y}) = \text{Tr}(\mathbf{y}\mathbf{x}))$ for arbitrary density matrices \mathbf{x} and \mathbf{y} . Eq. 10 states that the interaction between \mathbf{T}_k and \mathbf{P} (through the effective solvent potential operator) is zero. Therefore, enforcing Eq. 10 is equivalent to reducing the SS model to the VE model. $\mathbf{V}_S(\mathbf{T}_k)$ will then have no effect in the GS SCF calculation. In the following study, we formulate analytical gradients only for the LR and VE model because the essential element of the SS model, where the GS SCF calculation involves the effective solvent potential corresponding to the ES charge density, is lost in this variational formulation.

III. VARIATIONAL EXCITATION ENERGY EXPRESSIONS

A. Vacuum formalism and addition of the linear response solvent model

Throughout this and later sections, the algebra and formalisms for the TD-SCF equations described in detail in Ref. 61 are used.^{5,6,25,62–64} This formalism is often referred to as the collective electronic oscillator method and is equivalent to other formulations of the TD-HF and TD-DFT equations.^{25,65} To clearly state notation, the following relations are given. The bra-ket notation around a matrix (here also a double arrow) denotes tensorial mapping⁶⁶ of the interband partitions,

$$|\xi\rangle = \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = |\mathbf{X}, \mathbf{Y}\rangle \Leftrightarrow \begin{pmatrix} \mathbf{0} & \mathbf{Y} \\ \mathbf{X} & \mathbf{0} \end{pmatrix} = \boldsymbol{\xi}. \quad (12)$$

The conjugate of a tensorially mapped interband matrix such as $\boldsymbol{\xi}$ invokes a sign change, e.g.,

$$\langle \xi| = (\vec{X}, -\vec{Y}) = \langle \mathbf{X}^\dagger, -\mathbf{Y}^\dagger| \Leftrightarrow \begin{pmatrix} \mathbf{0} & \mathbf{X}^\dagger \\ -\mathbf{Y}^\dagger & \mathbf{0} \end{pmatrix} = [\mathbf{P}, \boldsymbol{\xi}^\dagger]. \quad (13)$$

where the commutator with \mathbf{P} is used to change the sign of \mathbf{Y} . These relations greatly simplify the algebra of the TD-SCF equations.

The Coulomb-exchange and exchange-correlation term for the TD-SCF equations $\mathbf{G}(\mathbf{x})$ is given by

$$G_{ij\sigma}(\mathbf{x}) = J_{ij\sigma}(\mathbf{x}) - K_{ij\sigma}(\mathbf{x}) + \sum_{kl\sigma'} f_{ij\sigma,kl\sigma'}^{xc} x_{kl\sigma'}, \quad (14)$$

where the f^{xc} kernel is a functional derivative of the exchange-correlation potential v^{xc} from Eq. 3. Similar to the GS SCF equations, TD-HF is recovered when c_x is set to one and f^{xc} to zero. A free energy functional, \mathcal{G} for the TD-SCF equations in vacuum,^{26,61} can now be defined using the Liouville space super-operator \mathbb{L} and the Lagrange multiplier Ω ,

$$\mathcal{G}(\mathbf{P}, \boldsymbol{\xi}, \Omega) = \langle \xi | \mathbb{L} | \xi \rangle + \Omega(1 - \langle \xi | \xi \rangle). \quad (15)$$

The standard \mathbb{L} in a vacuum is given by

$$\mathbb{L}|\mathbf{x}\rangle \Leftrightarrow [\mathbf{F}(\mathbf{P}), \mathbf{x}] + [\mathbf{G}(\mathbf{x}), \mathbf{P}]. \quad (16)$$

where tensorial mapping was defined in Eq. 12. Variation of $\mathcal{G}(\mathbf{P}, \boldsymbol{\xi}, \Omega)$ with respect to $\langle \xi|$ in Eq. 15 gives the well known RPA eigenvalue equation²⁶ in the Liouville space

representation,⁴¹

$$\frac{\partial \mathcal{G}}{\partial \langle \xi |} = \mathbb{L}|\xi\rangle - \Omega|\xi\rangle = 0, \quad (17)$$

where Ω is now defined as the excitation energy.

Variation of $\mathcal{G}(\mathbf{P}, \boldsymbol{\xi}, \Omega)$ with respect to Ω gives the RPA normality condition from the inner product,⁶¹ defined by

$$\langle \xi | \xi \rangle = \vec{X}^2 - \vec{Y}^2 = 1. \quad (18)$$

Upon optimization with respect to the parameters $\boldsymbol{\xi}$ and Ω , i.e. insert Eqs. 17 and 18 in Eq. 15, \mathcal{G} is equivalent to the excitation energy given by

$$\Omega = \langle \xi | \mathbb{L} | \xi \rangle. \quad (19)$$

The extension of the vacuum formalism (Eq. 15) to the LR solvent model has been performed elsewhere.³⁰ It requires replacement of the vacuum Liouville-space operator \mathbb{L} with the LR Liouville-space operator \mathbb{L}_{LR} , given by

$$\mathbb{L}_{LR}|\mathbf{x}\rangle \Leftrightarrow [\mathbf{F}_{LR}(\mathbf{P}), \mathbf{x}] + [\mathbf{G}(\mathbf{x}), \mathbf{P}] + [\mathbf{V}_S(\mathbf{x}), \mathbf{P}]. \quad (20)$$

This results in the same substitution of \mathbb{L} in Eq. 17 with \mathbb{L}_{LR} .

B. Vertical Excitation Model

For the VE model, the free energy functional becomes

$$\mathcal{G}_{VE}(\mathbf{P}, \boldsymbol{\xi}, \Omega) = \langle \xi | \mathbb{L}_{VE} | \xi \rangle - \frac{1}{2} \langle \xi | [\mathbf{V}_S(\mathbf{T}_k), \boldsymbol{\xi}] \rangle + \Omega(1 - \langle \xi | \xi \rangle). \quad (21)$$

where \mathbb{L}_{VE} is defined as

$$\mathbb{L}_{VE}|\mathbf{x}\rangle \Leftrightarrow [\mathbf{F}_{LR}(\mathbf{P}), \mathbf{x}] + [\mathbf{G}(\mathbf{x}), \mathbf{P}] + [\mathbf{V}_S(\mathbf{T}_k), \mathbf{x}]. \quad (22)$$

Variation of $\mathcal{G}_{VE}(\mathbf{P}, \boldsymbol{\xi}, \Omega)$ with respect to Ω results in Eq. 18, while variation with respect to $\boldsymbol{\xi}$ results in

$$\frac{\partial \mathcal{G}_{VE}}{\partial \langle \xi |} = \mathbb{L}_{VE}|\xi\rangle - \Omega|\xi\rangle = 0. \quad (23)$$

As detailed in Ref. 49, using the VE model evokes iterative solution of this equation to convergence of the solvent polarization and Ω . If this equation is not solved to convergence, e.g. performing only one iteration of solution of \mathbf{T}_k and $|\xi\rangle$ similarly to what has been

called the corrected LR model in the literature,^{67,68} a variational formulation and analytical gradient would not be possible since the dependence of \mathbf{T}_k on $|\xi\rangle$ would be unknown. We note that using an unconverged result will give unpredictable results since the speed of convergence is system dependent.

In contrast to vacuum and LR formulations, $\mathcal{G}_{VE} \neq \Omega$ after optimization, where Ω is given here by Eq. 19 using \mathbb{L}_{VE} . The optimized free energy functional \mathcal{G}_{VE} is instead equal to Ω' given by

$$\Omega' = \Omega - \frac{1}{2} \text{Tr}(\mathbf{T}\mathbf{V}_S(\mathbf{T}_k)). \quad (24)$$

The quantity Ω' does not occur in the LR model because the VE effective solvent potential is of second order in ξ while the LR effective solvent potential is of first order.

The variational excitation energy expression for the VE model, Eq. 24, is obtained by calculating the eigenvalues of \mathbb{L}_{VE} and then subtracting the energy correction from Ω . This resembles the calculation of E_{gr} from Eq. 6. The correction is not half of the total solvation energy, but rather half of the part of the solvation energy arising from the interaction (through the effective solvent potential) between an unrelaxed difference density and the unrelaxed difference density of state k . The portion of the solvation energy which does not enter this correction corresponds to the term $\text{Tr}(\mathbf{T}\mathbf{V}_S(\mathbf{P}))$. For the LR and VE models, $\partial\Omega/\partial\mathbf{P}$ or $\partial\Omega'/\partial\mathbf{P}$ must also be set to zero. This is achieved using the Z-vector technique described in section IV.

IV. VARIATIONAL EXCITED STATE ENERGY EXPRESSION

The ES energy is defined as $E = E_{gr} + \Omega$ for both the vacuum and LR formulations and $E = E_{gr} + \Omega'$ for the VE formulation. An expression for the ES energy can be made stationary with respect to variation of \mathbf{P} by use of the Z-vector technique.^{69,70} To do so requires enforcing stationarity of \mathbf{P} upon variation of Ω . Here, we generally follow the methods of Furche and Aldrichs²⁶, but vary \mathbf{P} rather than the molecular orbital coefficients. As with the rest of the main body of this publication, an orthogonal atomic orbital basis is assumed, but explicit results for a nonorthogonal basis are given in Appendix A.

A matrix of Lagrange multipliers \mathbf{Z} enforces stationarity with respect to variations in \mathbf{P} . A modified free energy functional is given by

$$\mathcal{J}(\mathbf{P}, \xi, \mathbf{Z}, \Omega) = \mathcal{G}(\mathbf{P}, \xi, \Omega) + \langle \mathbf{Z} | [\mathbf{F}(\mathbf{P}), \mathbf{P}] \rangle. \quad (25)$$

The added term is zero because $[\mathbf{F}(\mathbf{P}), \mathbf{P}] = 0$ so that the minimized functional is still equivalent to the excitation energy. Variation with respect to \mathbf{P} gives an equation for \mathbf{Z} . The condition leading to this is

$$\frac{\partial \mathcal{J}}{\partial \mathbf{P}} = 0 = \langle \xi | \frac{\partial \mathbb{L}}{\partial \mathbf{P}} | \xi \rangle + \langle Z | \frac{\partial [\mathbf{F}(\mathbf{P}), \mathbf{P}]}{\partial \mathbf{P}} \rangle. \quad (26)$$

where the matrix by matrix partial derivative is a fourth-order tensor given by $(\partial \mathbf{x} / \partial \mathbf{y})_{nm,jk} = \partial x_{nm} / \partial y_{jk}$. Carrying out the differentiation of the second term on the right hand side, the result is concisely written as

$$\mathbb{L}|Z\rangle \Leftrightarrow [\langle Z | \frac{\partial [\mathbf{F}(\mathbf{P}), \mathbf{P}]}{\partial \mathbf{P}} \rangle, \mathbf{P}]. \quad (27)$$

One may substitute the appropriate \mathbf{F} and Liouville-space operator into Eq. 26 and rearrange to obtain a system of linear equations. In vacuum, this process results in

$$\mathbb{L}|Z\rangle \Leftrightarrow -[\langle \xi | \frac{\partial \mathbb{L}}{\partial \mathbf{P}} | \xi \rangle, \mathbf{P}] = -[[[\mathbf{P}, \boldsymbol{\xi}^\dagger], \tilde{\mathbf{G}}(\boldsymbol{\xi})] + \mathbf{G}(\mathbf{T}), \mathbf{P}] \quad (28)$$

where $\tilde{\mathbf{G}}$ involves the functional derivative of f^{xc} given by g^{xc} , i.e.

$$\tilde{G}_{ij\sigma}(\mathbf{x}) = J_{ij\sigma}(\mathbf{x}) - K_{ij\sigma}(\mathbf{x}) + \sum_{kl\sigma'} g_{ij\sigma,kl\sigma',mn\sigma''}^{xc} x_{kl\sigma'} x_{mn\sigma''}. \quad (29)$$

For LR and VE solvent models, substituting with \mathbb{L}_{LR} or \mathbb{L}_{VE} and $\mathbf{F}_{LR}(\mathbf{P})$ gives the following Z-vector equations,

$$\mathbb{L}_{LR}|Z\rangle \Leftrightarrow -[\langle \xi | \frac{\partial \mathbb{L}_{LR}}{\partial \mathbf{P}} | \xi \rangle, \mathbf{P}] = -[[[\mathbf{P}, \boldsymbol{\xi}^\dagger], \tilde{\mathbf{G}}(\boldsymbol{\xi}) + \mathbf{V}_S(\boldsymbol{\xi})] + \mathbf{G}(\mathbf{T}) + \mathbf{V}_S(\mathbf{T}), \mathbf{P}]. \quad (30)$$

for the LR model and

$$\mathbb{L}_{LR}|Z\rangle \Leftrightarrow -[\langle \xi | \frac{\partial \mathbb{L}_{VE}}{\partial \mathbf{P}} | \xi \rangle, \mathbf{P}] = -[[[\mathbf{P}, \boldsymbol{\xi}^\dagger], \tilde{\mathbf{G}}(\boldsymbol{\xi})] + \mathbf{G}(\mathbf{T}) + \mathbf{V}_S(\mathbf{T}) + \frac{1}{2}[[\boldsymbol{\xi}_k, \mathbf{V}_S(\mathbf{T})], \boldsymbol{\xi}_k^\dagger], \mathbf{P}] \quad (31)$$

for the VE model.

The third term on the right hand side of Eqs. 30 and 31, appearing in both LR and VE model Z-vector equations, is a result of the solvent effects in the GS SCF calculation, i.e. the solvent shift of the molecular orbital energies. The fourth term on the right hand side of Eq. 31 is the result \mathbf{T}_k explicitly depending on \mathbf{P} as written in Eq. 9. This term results from the variation given by

$$\mathbf{T}(\delta \mathbf{P}, \boldsymbol{\xi}_k) = [[\boldsymbol{\xi}_k^\dagger, \delta \mathbf{P}], \boldsymbol{\xi}_k] \quad (32)$$

and appears in the VE model equations since \mathbf{T}_k is used to polarize the solvent. As is shown numerically in Sec. VI, this is necessary for the variational formulation. Noting that E_{gr} and the excitation energy expressions are variational with respect to all involved density matrices, the analytical gradient expressions for the ES energy can be written.

V. ANALYTICAL GRADIENT EXPRESSIONS

With the variational ES energy expressions in hand, analytical gradients with respect to a nuclear coordinate R , or other parameter, are possible by noting that the chain rule gives

$$\frac{\partial \Omega}{\partial R} = \frac{\partial \mathcal{J}}{\partial R} = \sum_i \frac{\partial \mathcal{J}}{\partial \mathbf{x}_i} \frac{\partial \mathbf{x}_i}{\partial R} \quad (33)$$

for all parameters \mathbf{x}_i in \mathcal{J} . For all parameters \mathbf{x}_j ($j \in i$) made variational in the above procedure,

$$\frac{\partial \mathcal{J}}{\partial \mathbf{x}_j} = 0, \quad (34)$$

so that those terms do not contribute to the gradient. To be concise, we write the gradient as (R) , e.g., $\mathbb{L}^{(R)}$. With stationarity of the parameters of \mathcal{J} determined, the derivative of the excitation energy Ω or Ω' can be calculated according to

$$\Omega^{(R)} = \mathcal{J}^{(R)} = \langle \xi | \mathbb{L}^{(R)} | \xi \rangle + \langle Z | [\mathbf{F}^{(R)}(\mathbf{P}), \mathbf{P}] \rangle. \quad (35)$$

Introducing the notation $\mathbf{P}_\Delta = \mathbf{T} + \mathbf{Z}$ as the relaxed difference density, Eq. 35 is written as

$$\Omega^{(R)} = Tr(\boldsymbol{\xi} \mathbf{G}^{(R)}(\boldsymbol{\xi})) + Tr(\mathbf{P}_\Delta \mathbf{F}^{(R)}(\mathbf{P})) \quad (36)$$

for the vacuum formulation. For the LR model, this becomes

$$\Omega^{(R)} = Tr(\boldsymbol{\xi} \mathbf{G}^{(R)}(\boldsymbol{\xi})) + Tr(\mathbf{P}_\Delta \mathbf{F}^{(R)}(\mathbf{P})) + Tr(\boldsymbol{\xi} \mathbf{V}_S^{(R)}(\boldsymbol{\xi})) + Tr(\mathbf{P}_\Delta \mathbf{V}_S^{(R)}(\mathbf{P})). \quad (37)$$

Similarly, the analytical gradient for the corrected excitation energy of the VE model is given by

$$\Omega'^{(R)} = Tr(\boldsymbol{\xi} \mathbf{G}^{(R)}(\boldsymbol{\xi})) + Tr(\mathbf{P}_\Delta \mathbf{F}^{(R)}(\mathbf{P})) + Tr(\mathbf{P}_\Delta \mathbf{V}_S^{(R)}(\mathbf{P})) + \frac{1}{2} Tr(\mathbf{T} \mathbf{V}_S^{(R)}(\mathbf{T}_k)). \quad (38)$$

Analogous equations in the position and momentum basis are given in appendix B. For VE and LR models, the GS energy gradient is given by differentiation of Eq. 1 with substitution of $\mathbf{F}_{LR}(\mathbf{P})$ to give

$$E_{gr}^{(R)} = Tr(\mathbf{P} \mathbf{F}^{(R)}(\mathbf{P})) - \frac{1}{2} Tr(\mathbf{P} \mathbf{V}^{(R)}(\mathbf{P})) + \frac{1}{2} Tr(\mathbf{P} \mathbf{V}_S^{(R)}(\mathbf{P})). \quad (39)$$

These analytical gradients allow one to practically calculate molecular forces. The forces can, for example, be used to determine the molecular motion in dynamic simulations or optimize the molecular structure. Since the gradients of the energies with respect to all density matrices are zero, only the gradients of operators need to be calculated. The gradients of the effective solvent potential operators are given elsewhere for methods such as PCM⁵⁵ and conductor-like PCM,^{71,72} but may also be easily formulated for polarizable force-fields and other solvent models such as effective fragment potential methods^{73,74}, the langevin dipole model, or surface-constrained all atom solvent.^{75,76}

VI. NUMERICAL RESULTS

Numerical tests of these variational expressions and analytical gradients are performed for two realistic molecular systems using the semiempirical AM1 Hamiltonian in TD-HF theory. The molecules used in these examples are shown in Fig. 1. First, the variational expressions are tested by using a static electric field gradient. Second, the analytical gradients for movement of nuclei are tested using microcanonical ESMD.

A. Static Electric Field

The variational energy expressions can be tested with respect to variation of \mathbf{P} or $\boldsymbol{\xi}$ by including the effects of a static electric field. This is done numerically and compared with the analytical solution, i.e. the dipole moment of the relaxed or unrelaxed difference density matrix. The electric field, denoted by $\vec{\mathcal{E}}$, is introduced in either the GS SCF or TD-SCF calculations. When it is introduced into the GS SCF calculation, the effect on the TD-SCF calculation is the result of shifting of the GS molecular orbital energies. When introduced only into the TD-SCF calculation, the GS is calculated at zero field and the molecular orbital energies are not affected. Greater detail is available in Appendix C.

Since the electric field interacts with the molecule through its dipole moment, calculation of $\partial\Omega/\partial\vec{\mathcal{E}}$ by the finite difference method will reflect the dipole moment corresponding to \mathbf{T} when introduced in the TD-SCF calculation and \mathbf{P}_Δ when introduced in the GS SCF. Comparison of the numerical and analytical results test the formulations given in Sections III and IV.

The third singlet ES of coumarin (Fig. 1) is used for this analysis since it has significant solvent effects for both LR and VE models.⁴¹ Figure 2 shows a comparison of the numerical energy gradient with the analytical result. The analytical results for the vacuum, LR, and VE model equations match the respective numerical results, confirming that the variational expression given in this publication are indeed correct. For comparison, test of an incorrect solution where it is assumed that $\mathbf{T}_k(\delta\mathbf{P}, \boldsymbol{\xi}_k) = \mathbf{0}$ is also shown. The analytical gradient calculated under this assumption does not reproduce the numerical results. We now examine the energy gradient with respect to nuclear coordinates in ESMD.

B. Microcanonical excited state molecular dynamics

Using the analytical gradients presented in Sec. V, microcanonical ESMD can be performed. This method is described in detail elsewhere.^{1,6,77,78} Here, dynamics of the first singlet ES of *p*-nitroaniline, which has significant CT character, are explored. Figure 3 shows the ES energy as a function of time for several solvent potential strengths based on the dielectric constant ϵ in an Onsager type effective solvent potential given by

$$V_S(\mathbf{x}) = \frac{\epsilon - 1}{\epsilon + 0.5} R^{-3} \hat{\boldsymbol{\mu}} \cdot \text{Tr}(\hat{\boldsymbol{\mu}} \mathbf{x}). \quad (40)$$

Here, $\hat{\boldsymbol{\mu}}$ is the dipole operator and R is the cavity radius taken to be 5 Å. In these microcanonical dynamics, the total energy is conserved with or without the solvent model (Fig. C inset). This shows that the analytical gradients which are used to calculate the kinetic energy are formulated and implemented correctly.

A motion corresponding to an out of plane bending of the NO₂ substituent is observed in dynamics when the VE model is used. The excitation energy also decreases rapidly to nearly 0.1 eV by 30 fs for $\epsilon = 10$ (not shown). This occurs at a slower rate as ϵ is decreased. These results are now compared with experiment and theory from literature sources.

The first singlet ES of *p*-nitroaniline is well known to have significant CT character. The geometry relaxation in vacuum of the first singlet state of an analogous molecule, nitrobenzene, has been investigated using high accuracy calculations at the complete active space SCF (CASSCF) level.⁷⁹ It is dominated by an out of plane bending of the nitro group. Experimentally, it has been shown that internal conversion to the electronic GS occurs in both *p*-nitroaniline and nitrobenzene within a few hundred femtoseconds.^{80,81} This internal

conversion occurs more rapidly in water (0.3 ps) in comparison to dioxane (0.5 ps) where the former has a much larger static dielectric constant.⁸²

The out of plane bending observed in these dynamic simulations has not been taken into account in most theoretical studies of *p*-nitroaniline. In computational studies of the first singlet ES of nitrobenzene, only twisting of the nitro group has been explored.^{3,80} In one study, geometry relaxation performed with TD-DFT and the LR solvent model missed this out-of-plane bending motion entirely. This is in agreement with the simulations presented here, where those with the LR solvent model do not predict this motion (Fig. 3).³ However, an out of plane bending is present in dynamics with the VE model. In the simulations performed with the VE model, solvent assisted internal conversion is suggested by decay of the excitation energy to the first singlet ES to near zero in concert with the observed $-NO_2$ bending (not shown).

VII. CONCLUSION

Variational ES energy expressions and analytical gradients for TD-SCF methods with polarizable solvent effects have been formulated. Enforcing a variational energy expression in GS SCF equations with the SS solvent model reduces it to the VE model. To implement analytical gradients using the LR model, the application of Eqs. 20, 30 and 37 is necessary. To implement analytical gradients using the VE model, Eqs. 22 and 24, followed by Eqs. 31 and 38 are necessary. The use of the VE model in TD-SCF methods allows solvent effects on ES with CT character to be explored. This was demonstrated in the first singlet ES of *p*-nitroaniline using semiempirical model chemistry. Further developments using solvent models in TD-SCF methods will involve non-adiabatic simulations and nonequilibrium dynamic solvent effects, as well as implementations of other polarizable solvent models and force-fields in ESMD.

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Appendix A: Variational Excited State Energy Expression in a Nonorthogonal Basis

The free energy functionals given in Section IV are written in an orthogonal basis, e.g. those used for most semiempirical Hamiltonians. However, many nonorthogonal bases are used in TD-SCF methods. The extension of the variational ES energy expression is straightforwardly given by optimization with the free energy functional written as

$$\bar{\mathcal{J}}(\mathbf{P}, \boldsymbol{\xi}, \mathbf{Z}, \Omega, \mathbf{W}) = \mathcal{J}(\mathbf{P}, \boldsymbol{\xi}, \mathbf{Z}, \Omega) + \langle W | (\mathbf{S} - \mathbf{I}) \rangle \quad (\text{A1})$$

where \mathbf{W} is a matrix of Lagrange multipliers enforcing stationarity of the excitation energy with respect to the overlap matrix \mathbf{S} . In the molecular orbital basis, \mathbf{S} is equivalent to the identity matrix \mathbf{I} ,

$$S_{nm} = S_{mn} = \langle \phi_n | \phi_m \rangle = \delta_{nm}. \quad (\text{A2})$$

Importantly, we note that S_{nm} is symmetric and thus \mathbf{W} is also required to be symmetric. \mathbf{W} spans both inter- and intraband space. The variational condition for \mathbf{W} is simply the orthonormality ensured by the GS SCF calculation.^{24,51,52} When the atomic orbital basis is also orthonormal, the Lagrange multipliers \mathbf{W} are not necessary because any gradient of the overlap matrix will be zero, e.g. $\mathbf{S}^{(R)} = 0$ in an orthogonal atomic orbital basis.

An extensive derivation of analogous equations are available in Ref. 26. We avoid using the atomic orbital basis explicitly here and write

$$\frac{\partial \bar{\mathcal{J}}}{\partial \mathbf{P}} = \frac{\partial \mathcal{J}}{\partial \mathbf{P}} + \langle W | \frac{\partial \mathbf{S}}{\partial \mathbf{P}} \rangle = 0 \quad (\text{A3})$$

where $\partial S_{nm} / \partial P_{jk} = \delta_{nj} \delta_{mk}$. \mathbf{W} now becomes

$$\mathbf{W} = -\frac{\partial \mathcal{J}}{\partial \mathbf{P}} \quad (\text{A4})$$

where one can substitute the various definitions of \mathcal{J} based on the desired solvent model, i.e. LR or VE, from that given here in vacuum.

We can now determine \mathbf{Z} in the nonorthogonal basis from this equation. Using the symmetries of \mathbf{W} and \mathbb{L} , i.e. that \mathbf{W} is symmetric and that \mathbb{L} is asymmetric, the solution for \mathbf{Z} is made independent of \mathbf{W} by writing

$$W_{ia\sigma} - W_{ai\sigma} = \mathbb{L}(\mathbf{Z})_{ia\sigma} - \mathbb{L}(\mathbf{Z})_{ai\sigma} + Q_{ai\sigma} - Q_{ia\sigma} = 0 \quad (\text{A5})$$

Here and in the following, a, b, c refer to occupied space and i, j, k refer to unoccupied space. \mathbf{Q} is given by

$$\mathbf{Q} = \langle \xi | \frac{\partial \mathbb{L}}{\partial \mathbf{P}} | \xi \rangle. \quad (\text{A6})$$

This shows that the system of linear equations for \mathbf{Z} in a nonorthogonal atomic orbital basis is nearly identical to those given in section IV except that the equations for the hole-particle space and particle-hole space are combined. One has thus also obtained the expression for the occupied-virtual and virtual-occupied blocks of \mathbf{W} . The occupied-occupied and virtual-virtual blocks of \mathbf{W} are obtained from

$$W_{ij} = Q_{ij} + G(\mathbf{Z})_{ij}; W_{ab} = Q_{ab} \quad (\text{A7})$$

by straightforward differentiation of Eq. A4.

The \mathbf{Z} -vector equation can also be written using the definition of the RPA matrix^{83–86} in terms of the tetradic \mathbf{A} and \mathbf{B} matrices^{26,65,87} as in Ref. 26

$$\sum_{jb\sigma'} (A + B)_{ia\sigma, jb\sigma'} (Z_{jb\sigma'} + Z_{bj\sigma'}) = -(Q_{ia\sigma} - Q_{ai\sigma}). \quad (\text{A8})$$

We explicitly write the hole-particle and particle-hole parts of $Z_{jb\sigma'}$ here, while in Ref. 26 sums them implicitly, leading to some differences in the form of \mathbf{Q} .

Determining \mathbf{W} after \mathbf{Z} has been determined requires only expanding the blocks of \mathbf{Q} and $\mathbb{L}(\mathbf{Z})$. For the vacuum formulation, this is found in Ref. 26 while for the LR formalism it is found in Ref. 30.

The use of the \mathbf{Z} -vector technique with the VE model is not found elsewhere in the literature. To connect with traditional notation, \mathcal{G}_{VE} must be written explicitly. Defining the additive part of \mathbf{Q} relevant to the VE model as $\mathbf{Q}^{VE} = \frac{1}{2}[[\boldsymbol{\xi}_k, \mathbf{V}_S(\mathbf{T})], \boldsymbol{\xi}_k^\dagger]$ from Eq. 31 and writing explicitly the blocks of \mathbf{Q}^{VE} while omitting the argument for $\mathbf{V}_S(\mathbf{T})$, this can be written as

$$Q_{ab}^{VE} = \frac{1}{2}(X_{ai}^k V_{ij}^S X_{bj}^k + Y_{ai}^k V_{ij}^S Y_{bj}^k - X_{ai}^k X_{ci}^k V_{cb}^S - V_{ac}^S Y_{ci}^k Y_{bi}^k) \quad (\text{A9})$$

$$Q_{ij}^{VE} = \frac{1}{2}(Y_{ai}^k V_{ab}^S Y_{bj}^k + X_{ai}^k V_{ab}^S X_{bj}^k - Y_{ai}^k Y_{ak}^k V_{kj}^S - V_{ik}^S X_{ak}^k X_{aj}^k) \quad (\text{A10})$$

$$Q_{ia}^{VE} = \frac{1}{2}(Y_{bi}^k V_{bj}^S X_{aj}^k + X_{bi}^k V_{bj}^S Y_{aj}^k - Y_{bi}^k Y_{bj}^k V_{ja}^S - V_{ib}^S Y_{bj}^k Y_{aj}^k) \quad (\text{A11})$$

$$Q_{ai}^{VE} = \frac{1}{2}(X_{aj}^k V_{jb}^S Y_{bi}^k + Y_{aj}^k V_{jb}^S X_{bi}^k - X_{aj}^k X_{bj}^k V_{bi}^S - V_{aj}^S X_{bj}^k X_{bi}^k) \quad (\text{A12})$$

where summation is implied by repeated indices. For $V_{ia}^S = V_{ai}^S$, the VE model part of the RHS of Eq. A8 is

$$\begin{aligned} -(Q_{ia}^{VE} - Q_{ai}^{VE}) &= \frac{1}{4} V^S(\mathbf{T})_{aj} [(X + Y)_{jb}^k (X - Y)_{bi}^k + (X - Y)_{jb}^k (X + Y)_{bi}^k] \\ &\quad + \frac{1}{4} V^S(\mathbf{T})_{ib} [(X + Y)_{jb}^k (X - Y)_{aj}^k + (X - Y)_{jb}^k (X + Y)_{aj}^k] \end{aligned} \quad (\text{A13})$$

which is the modification to the Z-vector equation in the notation of, e.g., the Casida equations⁶⁵ and relevant to the description of the position and momentum basis described in the following appendix.

Appendix B: Excitation Energy Gradient in the Position/Momentum Basis

In the basis of position ($|\mathbf{X} + \mathbf{Y}\rangle$) and momentum ($|\mathbf{X} - \mathbf{Y}\rangle$), the excitation energy is given by

$$\Omega^{(R)} = \frac{1}{2} \langle \mathbf{X}^\dagger + \mathbf{Y}^\dagger | (\mathbf{A} + \mathbf{B})^{(R)} | \mathbf{X} + \mathbf{Y} \rangle + \frac{1}{2} \langle \mathbf{X}^\dagger - \mathbf{Y}^\dagger | (\mathbf{A} - \mathbf{B})^{(R)} | \mathbf{X} - \mathbf{Y} \rangle. \quad (\text{B1})$$

Here, the so-called orbital rotation Hessians \mathbf{A} and \mathbf{B} are given by

$$\begin{aligned} (\mathbf{A} + \mathbf{B})_{ai\sigma,bj\sigma'} &= \delta_{ab} \delta_{ij} \delta_{\sigma\sigma'} (\epsilon_{a\sigma} - \epsilon_{i\sigma}) \\ &\quad + 2(ai\sigma|jb\sigma') + 2f_{ai\sigma,bj\sigma'}^{xc} - c_x \delta_{\sigma\sigma'} [(ja\sigma|ib\sigma + (ab\sigma|ij\sigma)] \end{aligned} \quad (\text{B2})$$

$$(\mathbf{A} - \mathbf{B})_{ai\sigma,bj\sigma'} = \delta_{ab} \delta_{ij} \delta_{\sigma\sigma'} (\epsilon_{a\sigma} - \epsilon_{i\sigma}) + c_x \delta_{\sigma\sigma'} [(ja\sigma|ib\sigma + (ab\sigma|ij\sigma)]. \quad (\text{B3})$$

This form is often used in other publications and is identical to the CEO formalism. The gradient of the excitation energy from Eq. 36 in a nonorthogonal basis is sometimes written as

$$\begin{aligned} \Omega^{(R)} &= \sum_{\mu\nu\sigma} t_{\mu\nu}^{(R)} P_{\mu\nu\sigma}^\Delta + \sum_{\mu\nu\sigma} S_{\mu\nu}^R W_{\mu\nu\sigma} + \sum_{\mu\nu\sigma} v_{\mu\nu\sigma}^{xc,(R)} P_{\mu\nu\sigma}^\Delta \\ &\quad + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} (\mu\nu|\kappa\lambda)^{(R)} \Gamma_{\mu\nu\sigma,\kappa\lambda\sigma'} + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} f_{\mu\nu\sigma,\kappa\lambda\sigma'}^{xc,(R)} (X + Y)_{\mu\nu\sigma} (X + Y)_{\kappa\lambda\sigma'} \end{aligned} \quad (\text{B4})$$

where the tetradic matrix $\mathbf{\Gamma}$ is the two particle difference density matrix given explicitly in Ref. 26. Here, $\mu, \nu, \kappa, \lambda$ refer to atomic orbitals. The goal here is to give the excitation energy gradients corresponding to Eq. 37 and Eq. 38 in the basis of position and momentum. We now write the additive term for this gradient for these solvent models. For the LR model, Eq. 37, this is adapted from Ref. 30 as

$$\Delta\Omega_{LR}^{(R)} = \sum_{\mu\nu\kappa\lambda\sigma\sigma'} \langle \mu\nu\sigma | \hat{V}_S | \kappa\lambda\sigma' \rangle^{(R)} P_{\mu\nu\sigma} P_{\kappa\lambda\sigma'}^\Delta + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} \langle \mu\nu\sigma | \hat{V}_S | \kappa\lambda\sigma' \rangle^{(R)} (\mathbf{X} + \mathbf{Y})_{\mu\nu\sigma} (\mathbf{X} + \mathbf{Y})_{\kappa\lambda\sigma'}. \quad (\text{B5})$$

For the VE model, Eq. 38, we can write

$$\Delta\Omega_{VE}^{(R)} = \sum_{\mu\nu\kappa\lambda\sigma\sigma'} \langle \mu\nu\sigma | \hat{V}_S | \kappa\lambda\sigma' \rangle^{(R)} P_{\mu\nu\sigma} P_{\kappa\lambda\sigma'}^\Delta + \sum_{\mu\nu\kappa\lambda\sigma\sigma'} \langle \mu\nu\sigma | \hat{V}_S | \kappa\lambda\sigma' \rangle^{(R)} T_{\mu\nu\sigma} T_{\kappa\lambda\sigma'}^k \quad (\text{B6})$$

where $\Delta\Omega^{(R)}$ has been written to signify the additive terms corresponding to the solvent model in the excitation energy gradient and the effective solvent potential has been written as an operator \hat{V}_S with the appropriate basis functions. For an example, see the appendix of Ref. 41.

Appendix C: Static electric field

A static electric field (EF) is included in the Fock or Kohn-Sham operator according to

$$\tilde{F} = F + \vec{\mathcal{E}} \cdot \hat{\mu}. \quad (\text{C1})$$

where $\hat{\mu}$ is the standard dipole operator and $\vec{\mathcal{E}}$ is the electric field vector. The interaction energy of the EF in the GS for a molecule in vacuum is $V_{\mathcal{E}} = \vec{\mathcal{E}} \cdot \vec{\mu}_{\mathbf{P}}$ and has a gradient of $\partial V_{\mathcal{E}} / \partial \vec{\mathcal{E}} = \vec{\mu}_{\mathbf{P}}$. By varying $\vec{\mathcal{E}}$ and calculating the gradient by the method of finite differences, we can obtain the GS dipole moments. This allows one to test the stationarity of the excitation energy with respect to variation of the \mathbf{P} . For variation of $\boldsymbol{\xi}$, the dipole moment of T can be obtained by calculating the ground state with F , but using \tilde{F} in the Liouville equation for $\boldsymbol{\xi}$. This is an artificial partitioning similar to the VE model. The gradient of the interaction energy is found to be

$$\delta\Omega / \delta \vec{\mathcal{E}} = \vec{\mu}_T \quad (\text{C2})$$

when the electric field is added to the Fock operator after the GS SCF equations are solved (before the TD-SCF calculation) and

$$\delta\Omega/\delta\vec{\mathcal{E}} = \vec{\mu}_{T+Z} \quad (\text{C3})$$

when it is added in the GS calculation. If the energy is nonstationary with respect to \mathbf{T} (Eq. B2) or both \mathbf{T} and \mathbf{P} (Eq. B3), deviation will occur.

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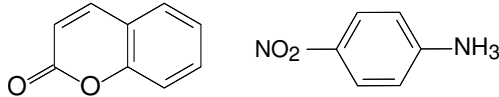


FIG. 1. Chemical structures used in numerical tests of variational formulations and analytical gradients. Left: coumarin, right: *p*-nitroaniline.

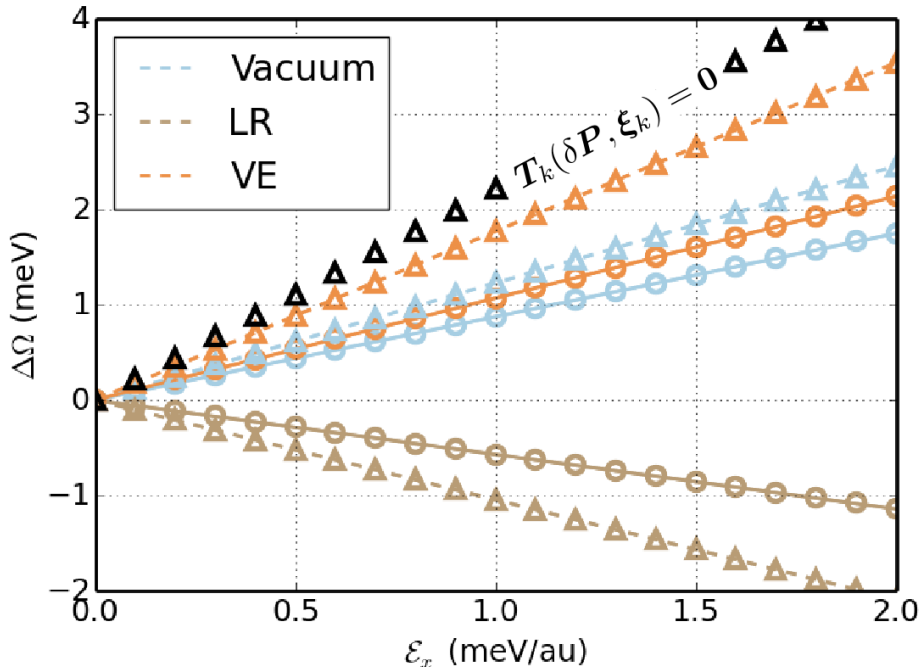


FIG. 2. Change in excitation energy $\Delta\Omega$ using electric field to perturb either the GS SCF (dashed) or TD-SCF (solid) calculations for the third singlet ES of coumarin. This ES exhibits strong solvent effects with both the LR and VE models.⁴¹ Calculations are performed with VE, LR, and vacuum. The circles are calculated according to $\Delta\Omega = \vec{\mathcal{E}} \cdot \vec{\mu}_T$ while the triangles use $\Delta\Omega = \vec{\mathcal{E}} \cdot \vec{\mu}_{T+Z}$ for dipole moments calculated at zero field with the dipole operator. Also pictured is a calculation assuming no variation in T_k with respect to \mathbf{P} in Eq. 31 (black triangles), which does not match the numerical simulations.

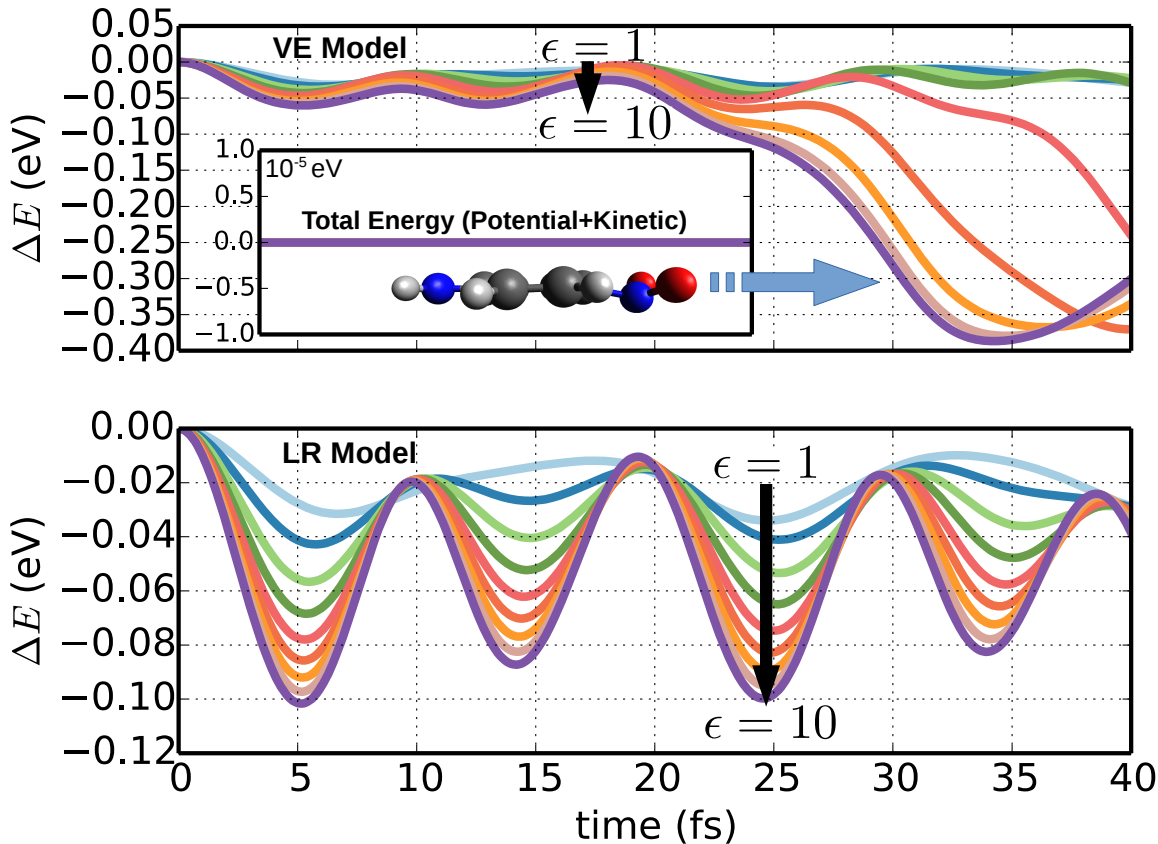


FIG. 3. Change in potential energy ΔE of first singlet ES during dynamics after photoexcitation for *p*-nitroaniline. These dynamics include the VE model (top) or the LR model (bottom) using an Onsager type potential. Light blue gives the dynamics in vacuum with increasing dielectric constant up to $\epsilon = 10$ in purple. The molecular conformation associated with the large decrease in E with the VE model at 40 fs is an out of plane bending of the nitro group. The inset shows the conserved total energy in the microcanonical dynamics, as expected for correct analytical gradients.